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ADSORPTION KINETICS OF PHENOLIC COMPOUNDS ONTO ACTIVATED CARBON

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ABSTRACT

Aqueous-phase adsorption equilibrium and kinetic mechanism of phenol, 3-chlorophenol and o-cresol onto Norit Granular Activated Carbon (NAC 1240) were studied in a batch system at temperature of 30 °C, agitation speed of 120 rpm, initial phenol concentrations of 25-200 mg/l. The effects of initial phenol concentration and time of adsorption on phenol adsorption process were investigated. The adsorption equilibrium data were reasonably fitted to Langmuir and Freundlich isotherm models over the entire range of initial concentrations used. The order of adsorption capacity among the phenolic compounds was o-cresol > 3-chlorophenol > phenol. Two simplified kinetic models, namely pseudo first-order equation and pseudo second-order equation, were selected to follow the adsorption processes. The adsorption of all adsorbates could be best described by the pseudo second-order equation. The kinetic parameters of this model were calculated and discussed.

Keywords: Adsorption, Phenolic compounds, Langmuir and Freundlich models, Activated carbon, Kinetic

I. INTRODUCTION

Organic pollutants, namely phenolic compounds are prominent generated by petrochemical, plastic, leather and paint industries, benzene refining plant and oil refineries. Wide ranges of phenol and chlorinated phenol have been found in the industrial wastewater stream. The contamination of surface and ground water by the aromatic compounds cause severe affect to the aquatic organism as well as human health. Phenolic compounds are potentially toxic to marine life. Although phenol has not been classified as carcinogenic to human but it is a known promoter of tumors. Besides, Environmental Protection Agency (EPA) recommends that the level of phenol in surface water (lakes, streams) should be limited to 3.5 mg/L to protect people from drinking contaminated water or eating contaminated fish. Human consumption of phenol-contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death [1]. Therefore, it is stringently obligatory to treat the waste stream to the required low limit of phenolic substance before it could be discharged to the environment. Several methods have been proposed in literature on techniques for removal of phenolic compounds from wastewater such as photocatalytic, microbial degradation, chemical-biological oxidation and catalytic oxidation process [2-6]. However, the adsorption process appears to be the most applicable method particularly for removing trace amount of contaminants from wastewater effluent [7].

Adsorption process is broadly used for removal of odor, oil, colours and organic contaminants from liquid-phase system. A variety of adsorbents have been used for removal of phenolic compounds, such as bentonite, fly ash, peat, saw dust, rice-husk, polymeric resin and organoclay [8-11]. However, the potential of granular and powdered activated carbon have been proven as an effective adsorbents used in adsorption technology over the century. Activated carbon provides large surface area, high adsorption capacity and high degree of surface reactivity [8]. However, the adsorption system relies on some other factors which include the nature of the adsorbate and adsorption condition such as pH and temperature. The physical properties of adsorbate depend on its polarity, hydrophobicity and molecular size [12, 13].

The objective of this work is to study the kinetics of adsorption of phenol, 3-chlorophenol and o-cresol from its aqueous solution onto commercial granular activated carbon.

II. MATERIALS AND METHOD

The adsorbent used was Norit Granular Activated Carbon 1240 (NAC 1240). This commercial activated carbon was supplied by Norit Nederland B.V., The Netherlands. The adsorbent was produced by steam activation of selected grades of coal and was used without any pretreatment or modification. The properties of NAC 1240 were characterized using Autosorb I (Quantachrome, USA) and are presented in Table 1. The activated carbon was dried overnight in the oven at temperature of 110°C to remove any moisture content. Phenol (>99.5% purity) was obtained from Merck (Germany) while 3-chlorophenol (>95% purity) and o-cresol (99.5% purity) were purchased from Fluka (Switzerland).

Single component laboratory test was conducted using conventional batch system. The stock of 1000 ppm solute solution was diluted to 8 different concentrations between 25-200 mg/l. A 0.2 g of adsorbent was added to a series of 250 ml glass-stoppered conical flasks filled with 200 ml diluted solutions. The glass-stoppered flasks were then placed in a water bath shaker and shaken at 120 rpm and constant temperature of 30 ± 1 °C. Shaking was continued until equilibrium condition was attained. Four ml of each aqueous-phase samples were taken out from the conical flasks at desired time interval and were analyzed using UV/V spectrophotometer (Shimadzu, UV-1601) to determine the remaining concentrations. The amount of solute adsorbed per unit weight of activated carbon (mg/g) was calculated according to the equation:

$$q_e = \frac{V(C_o - C_e)}{W} \tag{1}$$

where C_o and C_e are the initial and the equilibrium adsorbate-concentrations (mg/l), respectively, V is the volume of solution (l) and W is the weight of adsorbent (g).

Table 1: Properties of the commercial granular activated carbon, NAC 1240

Property	Value
Multi-point BET, m^2/g	7.783×10^2
Langmuir surface area, m^2/g	1.503×10^3
Average pore diameter, nm	2.716

III. THEORETICAL

1. Adsorption Isotherm

The adsorption isotherm defines the functional equilibrium distribution with concentration of adsorbate in solution at constant temperature. The adsorption equilibrium data were analyzed by Langmuir and Freundlich isotherm models. Both models are frequently used in literature to describe the relationship between the amount of solute adsorbed and its equilibrium concentration in solution for monolayer adsorption system. The Langmuir isotherm is valid for adsorption on a surface containing a finite number of identical sites. This model assumes that adsorption energy is constant and independent of surface coverage where the process mechanism occurs on localized site with no interaction between the adsorbate molecules. On the other hands, the Freundlich isotherm is used for heterogeneous surface energies in which capacity varies as a function of the surface coverage, due to variation in the heat of adsorption.

The linear form of Langmuir isotherm can be written as,

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ}\frac{1}{C_e} \tag{2}$$

where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), Q (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of $1/q_e$ versus $1/C_e$. The essential characteristics of the Langmuir equation can be expressed in terms of the dimensionless separation factor, R_L, defined as [14],

$$R_L = \frac{1}{(1 + bC_o)} \tag{3}$$

where, C_o is the highest initial solute concentration and b is the Langmuir's adsorption constant (l/mg). The R_L value implies that the adsorption is unfavorable (R_L>1), linear (R_L = 1), favorable (0 < R_L < 1), or irreversible (R_L = 0).

The linear form of the Freundlich isotherm model can be written as,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where K_F, (mg/g)(l/mg)$^{1/n}$ and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity of the sorbents, respectively. The values of K_F and $1/n$ can be obtained from the intercept and the slope, respectively, of the linear plot of ln q_e versus ln C_e.

Kinetic Models: In order to investigate the adsorption kinetics of phenolic compounds using activated carbon, two kinetic models were used, including pseudo-first equation and pseudo-second order equation. Additionally, the determination of a good model fitting provides an elementary functional used in predictive modeling procedure for water and wastewater treatment process design.

2. Pseudo First-Order Equation

A simple analysis of adsorption kinetic was applied to the experimental data obtained using pseudo first-order equation. The pseudo first-order equation is,

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{5}$$

where k_f is the rate constant of pseudo first-order equation and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial condition q_t = 0 at t=0 and q_t=q_t at t=t, the equation becomes [15]:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \tag{6}$$

Equation (6) is a linear form. Plotting log (q_e-q_t) against t permits calculation of k_f.

3. Pseudo Second-Order Equation

The pseudo second-order kinetic equation can be represented by the following equation [16]:

$$\frac{dq_t}{dt} = k_2(q_{eq} - q)^2 \tag{7}$$

where k_2 is the rate constant of the pseudo second-order equation. After integrating Equation 7 using the same initial conditions mentioned above, the following linear equation can be obtained:

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q} t \tag{8}$$

Plotting t/q against t, a straight-line can be obtained where k_2 also can be calculated.

IV. RESULTS AND DISCUSSION

1. Adsorption Isotherm

Figure 1 shows the adsorption isotherms of phenol, 3-chlorophenol and o-cresol onto NAC 1240. The equilibrium adsorption data were obtained at constant temperature of 30 ± 1 °C without any pH adjustment on the solute solution in order to prevent introduction of any new electrolyte into the system. The amount of adsorbent used was 1 mg/ml of adsorbate solution. The results show a typical nonlinear relationship between phenol uptake and equilibrium phenol concentration in solution which indicate favourable adsorption process. It is observed that the uptake of adsorbates increases with the increase in adsorbates concentrations. The initial solute concentration provides an important driving force to overcome all mass transfer resistance of adsorbate between liquid and solid phase. Therefore, by increasing the initial concentration of solute, higher interaction between adsorbate and adsorbent would occur and thus enhances the adsorption process. In addition, the curve fitting shows that the affinities of the phenolic compounds to the adsorbent are of the following order: phenol > 3-chlorophenol > o-cresol.

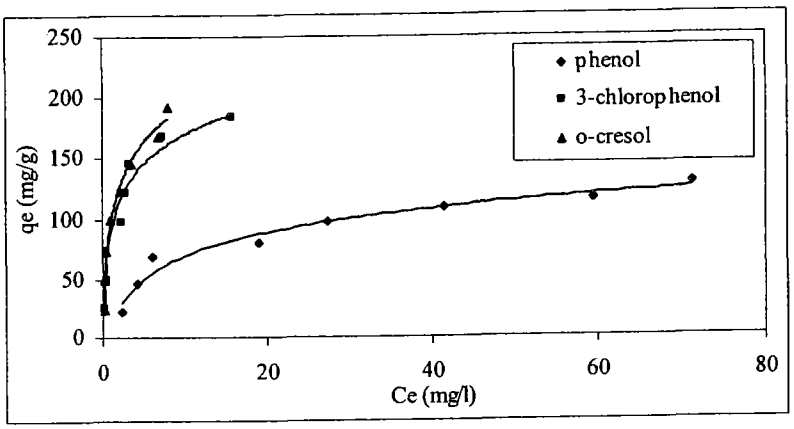

Fig. 1: Adsorption isotherm of phenolic compounds by NAC 1240 at 30 °C

The plots of Langmuir and Freundlich isotherms for different phenolic compounds are shown in Figures 2 and 3, respectively. Values of Q, b, K_F and n for different adsorbates are displayed in Table 2. Phenolic compounds adsorption onto activated carbon was generally well described by the Langmuir isotherm with correlation coefficient of $R^2 = 0.93$ or above. Results of Freundlich analysis (Table 2) indicate that the correlation coefficients are less than Langmuir analysis in describing the adsorption of phenolic compounds on the activated carbon. The present results were compared with several reported studies conducted on adsorption of phenolic compounds using various types of activated carbons [17-22] as shown in Table 3.

The values of the constant Q correspond to the maximum adsorption capacities of the activated carbon for the different adsorbates. Table 2 shows that the adsorption capacity of the activated carbon is higher for o-cresol followed by 3-chlorophenol and then phenol. The R_L values (Equation 3) indicate favorable adsorption, $0 < R_L < 1$. The data in Table 2 show that R_L values ranged between 0.004 to 0.062, indicating that the activated carbon are favorable for the three adsorbate considered in this work.

It is also apparent that the adsorption capacity, Q (mg/g), increased with the order of o-cresol > 3-chlorophenol > phenol. The nature of the adsorbates is the main factor that could be taken into consideration while explaining this behaviour. The phenolic compounds have a molecular size within the range of 0.8-1.0 nm [21] which is much

smaller than the average pore diameter of the NAC 1240 (Table 1). Thus, it is easy for phenols to penetrate into the inner pore of activated carbon and attach on the internal surfaces. In other words, the range of adsorbent pores is appropriate for phenols to be adsorbed and it is not an important factor in this case. However, the solubility of solute in the solvent/water has a significant effect on the adsorption process. The solubility of phenolic compounds in this study follows the order; phenol > 3-chlorophenol > o-cresol. Polar group has a high affinity for solvent/water. The higher of solute polarity as well as its solubility with the respect to the solvent used will decrease the tendency of adsorbate to be adsorbed from that aqueous phase. The bonding between adsorbate and water must be broken before the adsorption process can be occurred [13]. Basically, greater solubility provides stronger bonding between adsorbate and solvent/water. Thus, phenol, which is defined as a polar compound has higher solubility as compared to 3-chlorophenol and o-cresol, has the lowest adsorption capacity. The effect of solute solubility in water explained the adsorption capacity of phenolic compounds studied which followed the trend, phenol < 3-chlorophenol < o-cresol.

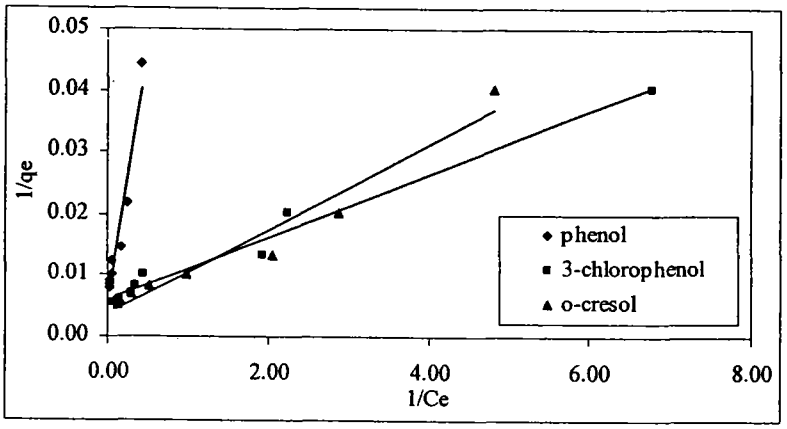

Fig. 2: Langmuir adsorption isotherm of phenolic compounds using NAC 1240 at 30°C.

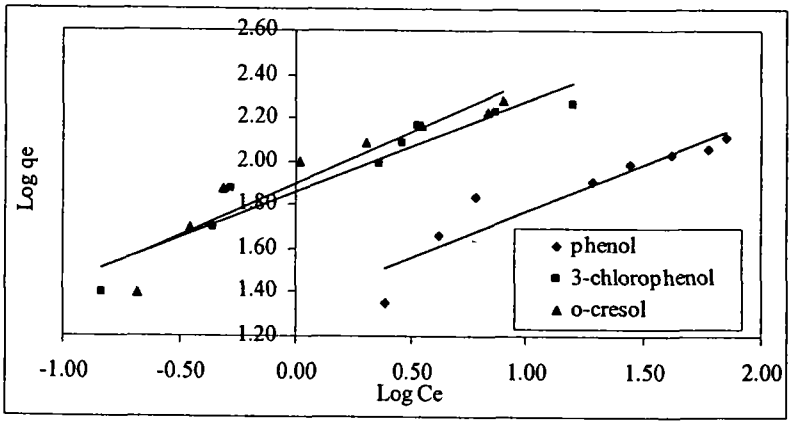

Fig. 3: Freundlich adsorption isotherm of phenolic compounds using NAC 1240 at 30°C.

Table 2: Langmuir and Freundlich constants for the adsorption of phenolic compounds using NAC 1240

Component	Langmuir Isotherm Model				Freundlich Isotherm Model		
	Q (mg/g)	b (l/mg)	R^2	R_L	K_F (mg/g) (l/mg)$^{1/n}$	n	R^2
Phenol	161.290	0.075	0.93	0.062	3.855	2.344	0.88
3-Chlorophenol	166.667	1.177	0.98	0.004	6.420	2.382	0.92
O-cresol	270.270	0.536	0.95	0.009	6.667	2.096	0.90

Table 3: Comparison of the maximum adsorption capacities of some phenolic compounds on various activated carbons

Phenolic compounds	Adsorbent	Maximum monolayer adsorption capacities (mg/g)	Ref.
Phenol	Norit 1240	161.290	This work
3Chlorophenol	Norit 1240	166.667	This work
O-cresol	Norit 1240	270.270	This work
Phenol	pinewood-based activated carbons	216.3	[17]
3-chlorophenol	pinewood-based activated carbons	314.2	[17]
O-cresol	pinewood-based activated carbons	275.5	[17]
Phenol	Activated carbon prepared from bagasse	250	[18]
Phenol	Activated carbon prepared from plum kernel	106	[18]
Phenol	Activated carbon prepared from corn cob	179	[18]
Phenol	AG D3016	180.59	[19]
Phenol	Original bituminous coal	152.0	[20]
3Chlorophenol	Original bituminous coal	206.4	[20]
Phenol	Demineralized bituminous coal	218	[20]
3Chlorophenol	Demineralized bituminous coal	234.4	[20]
		K_F, (mg/g)(l/mg)$^{1/n}$ in Freundlich Model	
Phenol	Norit RGM1	0.851	[21]
Phenol	Norit RB2	0.863	[21]
Phenol	Norit ROW0.8	1.452	[21]
Phenol	CGran	0.209	[21]
3Chlorophenol	AG D3016	2.078*	[19]
m-Cresol	AG D3016	1.8793*	[19]
Phenol	F400 washing with deionized water	49.3	[22]
Phenol	F400 washing with HCl	56.2	[22]

* The units are (mol/kg)(m^3/mol)$^{1/n}$

2. Validity of Kinetic Modeling

The validity of the two models can be checked from the linear plots of $\ln(q_e - q_t)$ vs. t and (t/q_t) vs. t, respectively. Tables 4-6 present the result of fitting experimental data with pseudo-first and pseudo-second-order equations.

Normalized standard deviation, Δq (%), is used to explore the most applicable model which could describe the kinetic study of adsorption of phenolic compounds on NAC 1240. The normalized standard deviation, Δq (%), was calculated using the following equation:

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum\left[\left(q_{t,\exp} - q_{t,cal}\right)/q_{t,\exp}\right]^2}{n-1}} \quad (10)$$

where n is the number of data points, $q_{t,exp}$ is the experimental values and $q_{t,cal}$ is the calculated values by model. From Tables 4-6, the order of Δq (%) was pseudo-first equation > pseudo-second order in most experimental conditions, which indicates that the pseudo-second order equation was better in describing the adsorption kinetics of phenolic compounds using granular activated carbon. Figure 4 typically illustrates the comparison between the calculated and measured results for adsorption of phenolic compounds for initial concentration of 100 mg/l. It is seen that the pseudo-second-order underestimates the experimental data at the initial stage (about 1-5 h) of phenol adsorption, while pseudo-first order equation underestimates for 3-chlorophenol and o-cresol adsorption. At the later stage (about 5-20 h), the pseudo-first-order underestimates the experimental data for 3-chlorophenol and o-cresol adsorption, while the pseudo-second-order underestimates the experimental data for phenol adsorption.

In many cases the pseudo-first-order equation does not fit well to the whole range of adsorption time and it is generally applicable only over the initial stage of the adsorption processes [15]. In addition, a good fitting of experimental data to pseudo-second-order equation suggests that the overall rate of adsorption process appears to be controlled by chemisorption process [15, 16].

Table 4: Kinetic parameters and normalized deviation for adsorption of phenol on NAC 1240

C_o, mg/l	Pseudo-First Order Equation		Pseudo-Second Order Equation		
	$k_f \times 10^{-1}$	Δq %	$k_s \times 10^{-3}$	q_e	Δq %
25	1.746	19.52	3.356	31.95	9.59
50	1.912	11.66	3.061	56.82	8.50
75	2.159	26.18	1.643	90.09	18.73
100	1.967	66.49	1.010	105.26	38.86
125	1.801	77.03	1.036	125.00	67.60
150	1.925	39.34	0.666	158.73	24.98
175	1.860	20.31	1.755	135.14	8.66
200	2.128	28.21	1.959	144.93	20.38

Table 5: Kinetic parameters and normalized deviation for adsorption of 3-chlorophenol on NAC 1240

C_o, mg/l	Pseudo-First Order Equation		Pseudo-Second Order Equation		
	$k_f \times 10^{-1}$	Δq %	$k_s \times 10^{-3}$	q_e	Δq %
25	2.897	17.13	0.151	27.62	4.34
50	2.693	7.92	3.983	59.17	3.88
75	3.163	23.40	5.241	81.97	15.55
100	2.636	18.66	2.348	116.28	28.24
125	2.619	33.59	1.765	147.06	44.10
150	1.832	40.51	2.962	158.73	8.97
172	2.180	36.07	2.677	181.82	11.41
200	1.992	31.18	1.656	204.08	16.52

Table 6: Kinetic parameters and normalized deviation for adsorption of o-cresol on NAC 1240

C_o, mg/l	Pseudo-First Order Equation		Pseudo-Second Order Equation		
	$k_f x\ 10^{-1}$	Δq %	$k_s x\ 10^{-3}$	q_e	Δq %
25	1.928	50.85	39.932	25.77	11.65
50	2.365	48.02	27.272	51.55	19.23
75	2.189	52.20	22.001	76.34	16.78
100	1.863	45.34	6.182	105.26	5.40
125	1.769	49.87	6.084	128.21	5.03
150	1.977	47.31	5.348	153.85	6.13
172	2.091	47.46	5.077	175.44	2.99
200	2.254	40.10	3.245	204.08	5.69

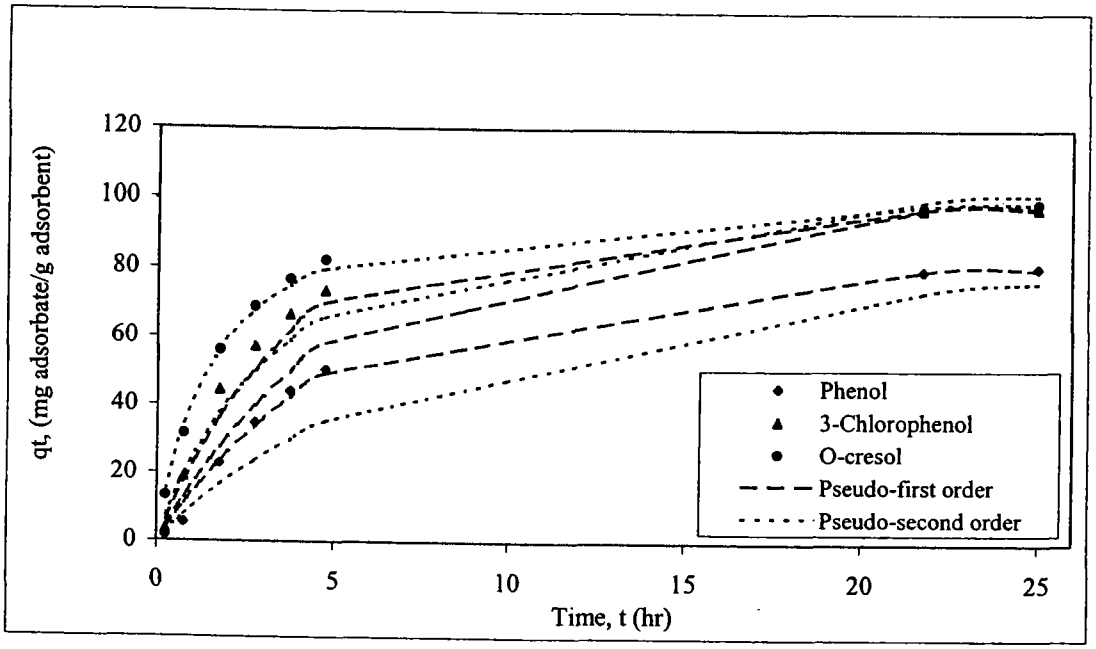

Fig. 4: Comparison between the experimental and modeled time profile for adsorption of phenolic compounds at 100 mg/l initial concentration

V. CONCLUSIONS

Phenol, 3-chlorophenol and o-cresol were found to adsorb strongly onto Norit Granular Activated Carbon (NAC 1240). The experimental batch study indicates that equilibrium time required for the adsorption of phenolic compound on NAC 1240 was almost 25 hours. Adsorption behavior of the three adsorbate-adsorbant systems was described well by Langmuir isotherm model. Two simplified kinetic equations, pseudo first-order equation and pseudo second-order equation, were selected to follow the adsorption processes. The pseudo second-order equation could better describe the adsorption of all adsorbates.

VI. ACKNOWLEDGMENT

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